## **Electronic Supplementary Information**

## Self-assembly of functionalized Echinops-like Rh porous

## nanostructure electrocatalysts for high efficient seawater splitting

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Fig. S1. UV-vis absorption spectra of PEI, RhCl<sub>3</sub>, and PEI+RhCl<sub>3</sub> solution.



Fig. S2. SEM image of Echinops-like Rh PNNSs.



Fig. S3. XPS full spectrum of Echinops-like Rh PNNSs.



Fig. S4. N1s XPS spectra of Echinops-like Rh PNNSs.



Fig. S5. TEM image of Rh nanostructures without PEI.



Fig. S6. TEM image of Rh aggregate synthesize with PEI 10000.



Fig. S7. TEM image of Rh aggregate synthesize by hydrothermal method.



**Fig. S8.** (a) HER polarization curves of Echinops-like Rh PNNSs in the electrolyte of simulating seawater and natural seawater at a scan rate of 5 mV s<sup>-1</sup>, (b) comparison of overpotential to drive a current density of 10 mA cm<sup>-2</sup> and mass-specific activity (jm) at -0.1 V (vs. RHE) in simulating seawater and natural seawater, and (c) corresponding Tafel plots.



**Fig. S9.** Cyclic voltammograms of (a) Echinops-like Rh PNNSs and (b) Pt black in the region of 0.6-0.75 V vs RHE at the scan rates of 20, 40, 60, 80, 100, 120 mV/s.



Fig. S10. The TEM image of homemade Rh bulk.



**Fig. S11.** HER polarization curves of homemade Rh bulk before and after 1000 cycles.



**Fig. S12.** EIS spectrum of Echinops-like Rh PNNSs in 1.0 M PBS solution, simulating seawater, and natural seawater.



Fig. S13. Chronopotentiometry curve of Echinops-like Rh PNNSs and  $RuO_2$  for OER without iR compensation.



**Fig. S14.** OER polarization curves of Echinops-like Rh PNNSs and commercial RuO<sub>2</sub> before and after long-term continuous tests in 1.0 M PBS solution.



**Fig. S15.** XPS full spectrum of Echinops-like Rh PNNSs after long-time durability at the anode.



**Fig. S16.** XPS full spectrum of Echinops-like Rh PNNSs after long-time durability at the cathode.



**Fig. S17.** XPS spectra of the oxidation of metallic Rh on the surface of Echinops-like Rh PNNSs



**Fig. S18.** TEM image of Echinops-like Rh PNNSs after long-time durability at the anode.



**Fig. S19.** TEM image of Echinops-like Rh PNNSs after long-time durability at the cathode.